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Features of Graft Copolymer Formation Through Reaction of Functionalized Polyolefins With Poly-ϵ-Caprolactam

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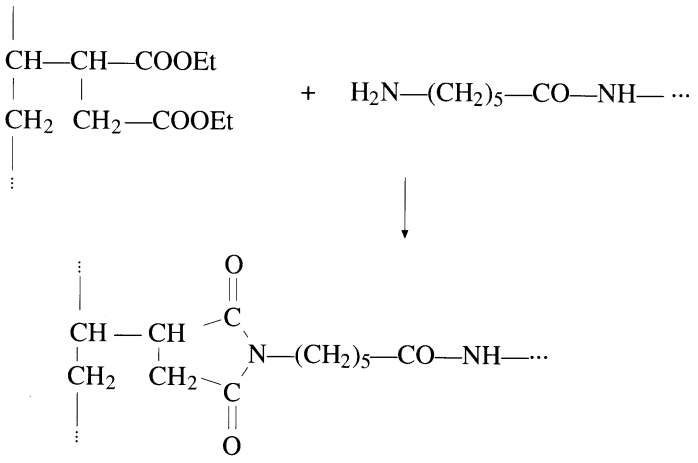
The reaction in the melt of polyolefins containing 2-diethylsuccinate groups (DES) with poly-ϵ-caprolactam (PA6) to give a graft copolymer was investigated under different conditions. Even using a large excess of DES groups over the PA6 terminal amino groups the graft copolymer yield resulted only partial thus suggesting a kinetic control of the reaction. The effect of various catalysts was then examined taking into account results obtained in a model reaction between a low molecular weight amine and diethylsuccinate. The results are discussed in terms of side reactions and miscibility of the pristine polymers.

Introduction

It is we known that maleic anhydryde functionalized polyolefins can react with amino-terminated polyamides to give graft copolymer macromolecules[1-5]. The same reaction can be expected (Scheme 1) with polyolefins containing 2-diethylsuccinate groups (DES) formed by free radical functionalization of the polyolefin with diethylmaleate (DEM)[6]. Also in this last case the reaction takes place simply in the melt at about 220° C[7] and can be carried out in a controlled way even in a Brabender mixer[8]. However even using a large molar excess of DES (ester/NH_2 = 4.3 ÷ 26.3) groups only a fraction of the PA6 was grafted to the polyolefin[9,10].

As this result could indicate a kinetic control of the process derived from a high activation energy and/or diffusion problems, it appeared of interest to use catalyst mainly to overcome the former problem. In the present paper sèveral catalysts of the reaction between carboxylate and amino groups were tested. The reaction between butylammine and diethylsuccinate was investigated in solution where diffusion problems could be disregarded. The same catalysts were then used in the intermacromolecular reaction in the melt and no substantial improvement of the grafted copolymer formation was observed, whereas evidences of side reaction catalysed by the above additives was observed thus supporting the predominant role of the limited diffusion in determining the graft copolymer yield.



Scheme 1. Reaction of DES groups (grated onto the polyolefin) with amino end groups of the polyamide

Experimental

Materials

The functionalized ethylene-propylene 70/30 copolymer (EPR-g-DES) was prepared in a Brabender mixer at 190 °C by radical functionalization with diethylmaleate (DEM) as monomer and dicumylperoxide (DCP) as radical initiator[8]. The functionalization degrees (FD) of the used samples were in the range of 1.7-1.9 % mol.

The Nylon 6 (PA6) having 22,000 number average molecular weight, 52 meq/KG - NH_2 and 45 meq/Kg-COOH as terminal groups was supplied by Snia Viscosa.

The reaction blending was carried out at 245 °C for 10 minutes with a 70/30 mixture of polyolefin to polyamide and 0.5 % wt of catalyst.

Model reactions

5 mL (3×10^{-2} mol) of diethylsuccinate, 6.1 mL (6×10^{-2} mol) of n-buthylamine and 20 mL of toluene were introduced in a round-bottom flask equipped with a refrigerator and a gas-cromatography septum as a cap. The mixture was heated to the refluxing temperature of about 78 °C and the catalytic system (3.07×10^{-3} mol) was added after 2 minutes. The mixture was then maintained at 78 °C for 1.5 hr while 0.1 mL fractions of the solution were extracted out using a syringe every 10 minutes. These fractions were analyzed by gas-cromatography and compared to standard solution of diethylsuccinate in toluene to evaluate the conversion of the ester group into amide.

Characterization

The reactions between EPR-g-DES and PA6 were performed under nitrogen atmosphere in a Brabender mixer (Plastograph) according to the following procedure. The two polymers (EPR-g-DES/PA6=70/30 w/w) and the catalyst were introduced in the mixer and the reaction was carried out at 245 °C for 10 minutes at 30 rpm.

The recovered polymer was sequentially extracted with formic acid at 50 °C for 120 hr and with boiling n-heptane for 24 hr.

The FT-IR spectra were recorded with a Perkin-Elmer DSC-7 under nitrogen atmosphere. The heating and cooling thermograms were carried out at standard rate of 20° C/min.

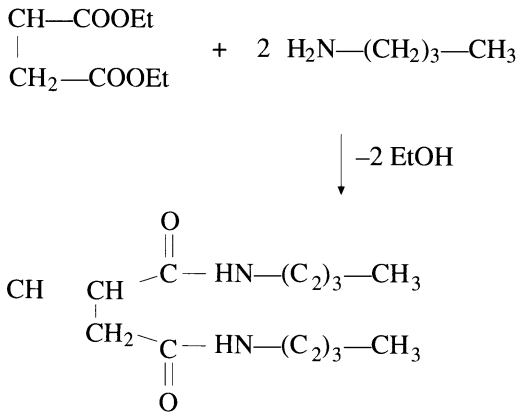
The TGA were performed with a Mettler TC11 under nitrogen atmosphere at a standard rate of 10° C/min.

Results

Model reactions

Greco et al.[11] reported that the reaction of 2-dibutylsuccinate (BDS) groups grafted onto an ethylene-propylene copolymer with trideclyammine in 1/10=DBS/-NH_2 molar ratio at 260° C gives the diamide, thus indicating that at such high temperature the formation of an amide bond and occur between an amine and a carboxylate functionality.

The same reaction has been now carried out starting with diethylsuccinate (as model of the DES carboxylate moieties grafter to the polyolefin) and n-butylamine in toluene solution. Working at DES/amine=1/2 molar ratio and at the refluxing temperature of the mixture (78° C) the reaction is rather slow with formation of the diamide (Scheme 2).



Scheme 2. Reaction of diethylsuccinate with n-butylamine.

However the reaction rate is very sensitive to the presence of 5% catalytic compound as shown in Table 1. Indeed the isoconversion time (10%) is much lower in the case of catalyzed reactions compared to the of the non-catalyzed one. The dramatic effect of the catalyst and the progress of the catalyzed reaction after the isoconversion time suggest an evident kinetic control for the reaction which seems to have not reached the equilibrium conditions after 10 minutes under the adopted conditions.

Reaction of the DES functionalised polyolefin and PA6

In case of the two polymeric reagents the reaction was carried out in the melt as previously reported[9,10]. In this case, differently from the model reacitons, a higher content of carboxylate groups was used with respect to the number of amino groups (DES/amino groups = 23 ÷ 26) as these last are limited by the high molecular weight of the polyamide. Under these conditions the reaction can be expected to proceed to the formation of the imide (Scheme 1) as the formation of the diamide needs a stoichiometric ratio 1/1-COOR to-NH_2 (Scheme 2). These conditions should favour the complete conversion of the amino groups from a thermodynamic viewpoint. However as the reaction is exothermic[12] one can expect a partial limitation from the high temperature necessary to keep the mixture in the molten state.

Table 1. Isoconversion[a] (20 %) time of the reaction between diethylsuccinate and butylamine

MD0	Catalyst	Isoconversion time (min)	Conversion (%)[a] after 10 min
MD0	none	1,200	n.d
MD1	NH_4Cl	10	10
MD5	LiCl	< 10	13
MD3	LiBr	< 10	25
MD6	LiI	< 10	47
MD4	KI	> 60	1

a: % of moles of ester groups reacted

The advancement degree of the reaction was evaluated on the basis of the residual polymer weight after the extraction with formic acid to remove the partially unreacted PA6 and n-heptane to remove the non reacted functionalized polyolefin[10]. The results of solvent extraction are reported in Table 2.

Table 2. Fractionation of reaction products deriving from the reactive blending of functionalized PO and PA6

Run	FD (% mol)	Catalyst	Molar ratio DES/ $-NH_2$	n-Heptane fraction (% wt)	Formic acid fraction (% wt)	Residue (% wt)	PA6 in the residue[a] (% wt)	Converted amino groups[b] (mol %)
FB0	1.9	none	26	52	12	36	47	60
FB1	1.8	NH_4Cl	25	54	21	25	34	30
FB2	1.8	Et_4NOTs[c]	25	59	20	21	45	32
FB3	1.7	LiBr	23	50	20	30	33	35
FB4	1.7	KI	23	54	19	27	39	40

a: calculated on the basis of mass balance and expressed as g of PA6 in the residue/(g of PO + g of PA6 in the residue)

b: calculated under the assumption of unchanged average length of PA6 chains

c: tetraethylammonium *p*-toluenesulfonate

The formic acid fraction (Figure 1) partially consists of pure PA6, while the n-heptane solution fractions consist of functionalized polyolefins (Figure 2) according to the uniform distribution of DES groups in the polyolefin macromolecules. Finally the IR spectra of the residue show (Figure 3) the presence of functionalized polyolfin and PA6.

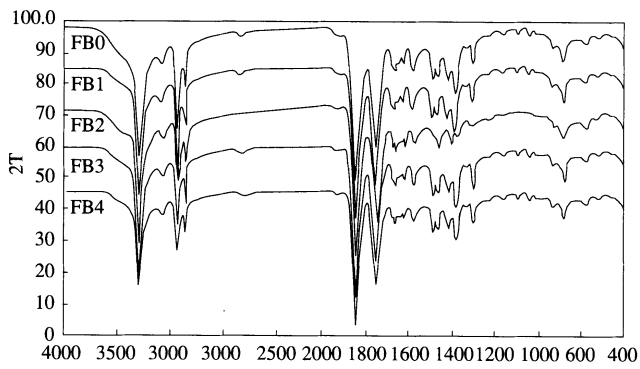


Figure 1. IR analysis of the fractions extracted with formic acid from the reaction products from functionalized PO and PA6

Then, in a first approximation, the percent weight of PA6 in the residue can be taken as a relative indication of the reacted PA6 amino groups, as the insolubility in the two previous solvents indicates the formation of graft-copolymer. This would imply that the reactivity of PA6 macromolecules is independent of molecular weight and no change of molecular weight distribution occurs during the reaction in the melt. This approximation is substantiated by the infrared analysis. Under this assumption an indicative comparison between the model reaction MD0-MD6 and that between the two polymers FB0-FB4, can be mode on the basis of the evaluated fraction of reacted amino groups in the different systems.

In the absence of catalyst the conversion of the amino groups is much more rapid [60 % of the PA6 free amino groups are converted into imide (or amide)] for te polymers that for the model reaction [1200 min to reach 20 % conversion], thus indicating the determining effect o fthe temperature, 245 and 78 °C respectively; inded the global concentration f reactive groups (amino and ester groups) in larger in the model reaction than in the polymeric system. However the intermacromolecular reaction does not reach the completeness. This is probably not due to thermodynamic reasons; indeed even if the reaction is exothermic, the molar ratio-COOEt/$NH_2 \approx 50$ should grant for the achivement of the thermodynamic equilibrium. Therefore a kinetic control should be claimed for the presence of unreacted PA chains (fraction extracted with formic acid) and the only partial formation of grafted copolymer (residue).

In apparent contrast with this consideration lower conversion was obtained by adding to the polymer system various catalysts which moreover all gave similar conversions (see Table 2). On the other side high accelaration and significative differences among catalytic species had been observed in the model reaction (see Table 1). The different situation is emphasized by the observation that the higher conversion for the polymeric system is obtained with KI as catalyst, which in the model reaction was the less active among those investigated.

These data demonstrate that the not complete conversion of free PA6 end amino groups, and thus the not complete grafting of PA6 chains to the polyolefin during the intermacromolecular reaction is probably not due to the too high activation energy of the amidation reaction in homogeneous phase. Rather one can assume that this arises from the heterogeneity of the reacting mixture with the partial entrapping of free amino groups in the PA6 domains in the not completely compatible blends. These groups are then not able to reach the interface with functionalized polyolefin domains where the amidation reaction reasonably occurs.

To substantiate this hypothesis the compatibility reached in the different experiments has been evaluated on the basis of the DSC analysis; indeed the fractionated crystallization of PA6 in the blend provides a valid indication of the mixing degree[13,14]. The presence of the catalyst causes an evident decrease of the compatible mixing as shown by the fact that larger amounts of PA6 crystallize at the regular temperature of 173-7 °C indicating that this component maintains its own characteristics (Table 3). In particular this effect is evident with the catalysts which are rather active in the transamidation reaction, which also activate the thermal decomposition of PA6. The last reaction is confirmed by the thermal analysis (see Figure 4 and Table 4) which indicates the starting of weight loss at lower temperatures attributable to the formation of volatile short PA6 fragments. Therefore under catalytic reaction at temperature high enough to make even the noncatalyzed reaction very rapid, the formation of short PA6 chains, due to the degradation activated by the catalyst gives polyolefins with short grafted chains which seem to be less effective in improving the mixing between the two different macromolecular species.

Table 3. DSC analysis of reaction products from functionalized PO and PA6

Run	T_m^a °C	ΔH_m J/g	T_c^b °C	ΔH_c J/g
FB0	221	17.6	176/107	0.3/10.8
FB1	221	17.8	176/100	14.4/3.2
FB1	219	17.0	176/100	5.5/6.5
FB3	221	19.0	173/106	7.6/4.8
FB4	222	19.8	177/107	6.9/6.9

a: melting temperature of the polyamide phase

b: crystallization temperature of the polyamide phase

Table 4. Thermogravimetric analysis of PA6 in the presence of catalytic systems

Catalyst	Catalyst amount (% wt)	Degradation temperature (°C)[a]
none	0	448
NH_4Cl	6	424
Et_4NOTs	7	399
LiBr	7	399
KI	4	424

a: temperature at which samples loose 50% of their initial weight

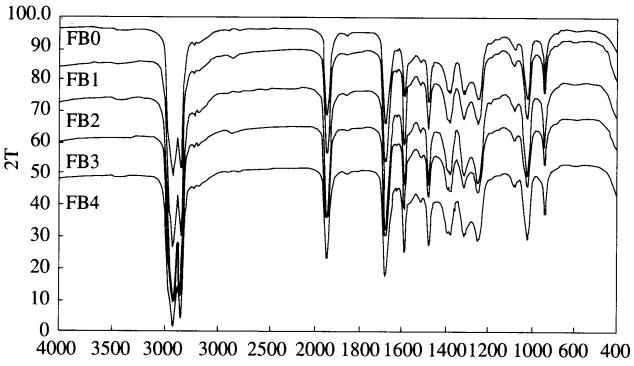


Figure 2. IR analysis of the fraction extracted with n-heptane from reaction products from functionalized PO and PA6

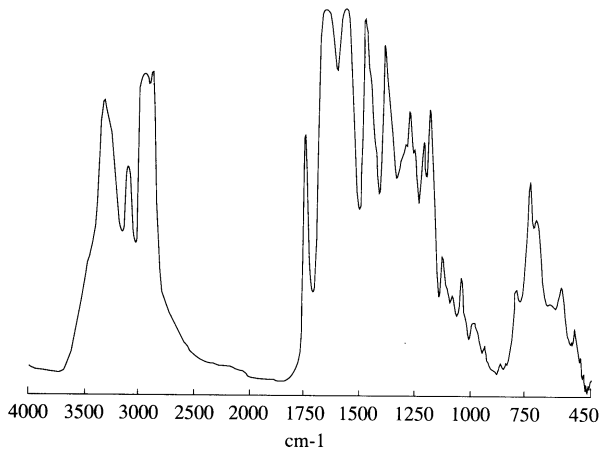


Figure 3. IR spectra of the residue to all extractions for the run FB1

Conclusions

The results described in this paper can be explained by considering that the added catalyst while activating the reaction between ester and amino groups (Scheme 1) also activates the degradation of PA6 chains (Scheme 3). This idea seems to be confirmed by the results of thermogravimetric analysis and should explain the diminished compatibility of the two components on adding the catalytic system. Indeed, if the degradation reaction for the polyamide is active and accelerated by the catalytic system, the average length of the polyamide chains grafted onto PO should be reduced producing an increase in the weight percentage of

formic acid fraction, a decrease in the weight percentage of the residue to all extraction and a decrease in the compatibility between the PO and the PA6, as shown by our results.

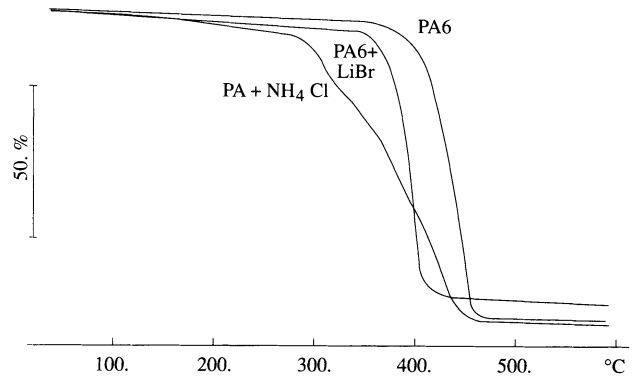
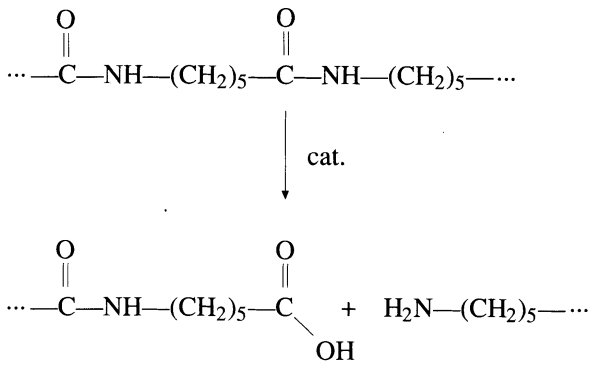


Figure 4. Thermogravimetric analysis of PA6 in the presence of some catalytic systems.



Scheme 3. Degradation reaction of the polyamide

The catalysts used in the present work are more compatible with the PA6 then the polyolefin. The use of catalysts more keen to take position at the interface between PA6 and the functionalized polyolefin is under investigation and will be subject of future papers.

Acknowledgements

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